

OST TECHNICAL PROGRESS REPORT FY 2001 RESULTS

TITLE: Fuel Processing Research Team

TEAM MEMBERS:

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DESCRIPTION: The role of the Fuel Processing Research Team is to develop new concepts involving fuel cleanup, reforming, conditioning, and process integration. The team serves as an incubation group for the development of new fuel processing concepts within the scope of the division and as a place to begin new chemical reaction-based research.

Team activities in FY 2001 focused on two of NETL's product lines: Gasification Technology and Fuel Cells. Five distinct efforts were undertaken this past year to support these product lines. The following is a list of these projects and a brief description of each:

- 1.) ***Conceptual design, simulation, and analysis of fuel processing technologies for solid state fuel cell systems*** - In FY 2001, NETL initiated a 10-year program for the development of mass manufactured, low-cost fuel cells based on solid oxide ion conductors. In order for this technology to be attractive in the near-term, it must be able to operate on current infrastructure fuels such as gasoline, diesel, or natural gas. This places a burden on fuel processors that must convert the fuel into a very clean hydrogen-rich synthesis gas that is required by the fuel cell. This particular activity evaluated the fuel processing requirements of specific applications to aid in developing research directions and technology needs for the program.
- 2.) ***Sulfur removal technology assessment and development for fuel cell systems*** - Many of the current infrastructure fuels contain sulfur, which is a poison to both reforming catalysts and fuel cell anode electrocatalysts. This activity focused on evaluating desulfurization technologies in general and assessing specific techniques through testing and development.
- 3.) ***Development of facility infrastructure for fuel processing*** - In order to conduct a comprehensive R&D program in fuel processing, the team continued activities on a mid-scale fuel processing research facility (FPRF) and a smaller-scale fuel processing laboratory (FPL).

- 4.) ***Simulation and modeling of transport desulfurizers*** - The use of transport reactors for the desulfurization of coal-gas from gasification processes has been supported by NETL for several years. This is an ongoing project to model those reaction systems and develop data to validate the models.
- 5.) ***Selective catalytic oxidation of hydrogen sulfide (SCOHS) process studies*** - The use of many hydrocarbon feeds in gasification processes involve a need to reduce/remove the sulfur contained in the feedstock. The SCOHS process is a one-step technology that both reduces the sulfur concentration to parts per billion (potentially) and produces an elemental sulfur byproduct stream that can sold as a commodity.

LONG TERM GOALS / RELATIONSHIP TO NETL'S PRODUCT LINE(S):

The long-term goal of the Fuel Processing Research Team is to support NETL's needs for fuel gas processing technology R&D through the establishment of technical expertise and comprehensive facilities to conduct the research. The Team's current focus is primarily in support of NETL's Gasification Technology and Fuel Cell Product Lines and is planned to continue for these long-term cornerstone programs. The cleanup technologies discussed, although being developed for those product lines, have the potential to be extrapolated to other product lines and industries that require fuel gas cleanup. Other market applications for developed technology will be continually assessed.

For gasification technology, a shift from electric power-only systems to systems that provide for fuels and chemicals has necessitated another look at syngas processing needs. The current zinc-based hot gas desulfurization sorbents provide for cleanup to the ppmv level. Cleanup of several compounds (especially sulfur) will require removal to the ppbv range to satisfy syngas catalyst and membrane separation requirements.

Fuel cells provide for very high efficiency power generation. NETL has been developing fuel cells for stationary power applications for many years. Most of these applications are for dispersed power, although baseload and gasification / fuel cell integrated systems are being evaluated. With the initiation of DOE's 10-year SECA fuel cell development program, many other applications and markets will likely be identified. The design specification or requirements for the fuel processing component for these cases will be site and application-specific and will need to be dealt with on an individual basis.

Finally, as environmental regulations become more and more stringent, cleanup and fuel gas processing needs will become increasingly important either in terms of efficiency and effectiveness or economics. The Fuel Processing Research Team will strive to provide the necessary R&D support.

PROJECT TITLE: *Development of Facility Infrastructure for Fuel Processing*

DESCRIPTION: Two distinct activities are currently being undertaken to provide facility/equipment capability for fuel processing R&D. The first is the fuel processing research facility (FPRF). Currently under construction, this multi-unit operation facility centers around a 30-foot long by 3-inch diameter electrically heated catalytic reformer. This reformer is U-shaped and is enclosed within a 20-foot tall pressure boundary. Nominal gas flows are estimated to be approximately 2000 scfh. Natural gas or vaporized liquid fuels are the planned feedstocks to the reactor and will undergo various reforming and cleanup unit operations. The facility, when constructed, will significantly augment NETL's complement of gas/solid contacting reactors and will provide for an economical means of conducting mid-scale fuel processing experiments. Figure 1 below is a pictorial of the FPRF and the various unit operations being included in the facility.

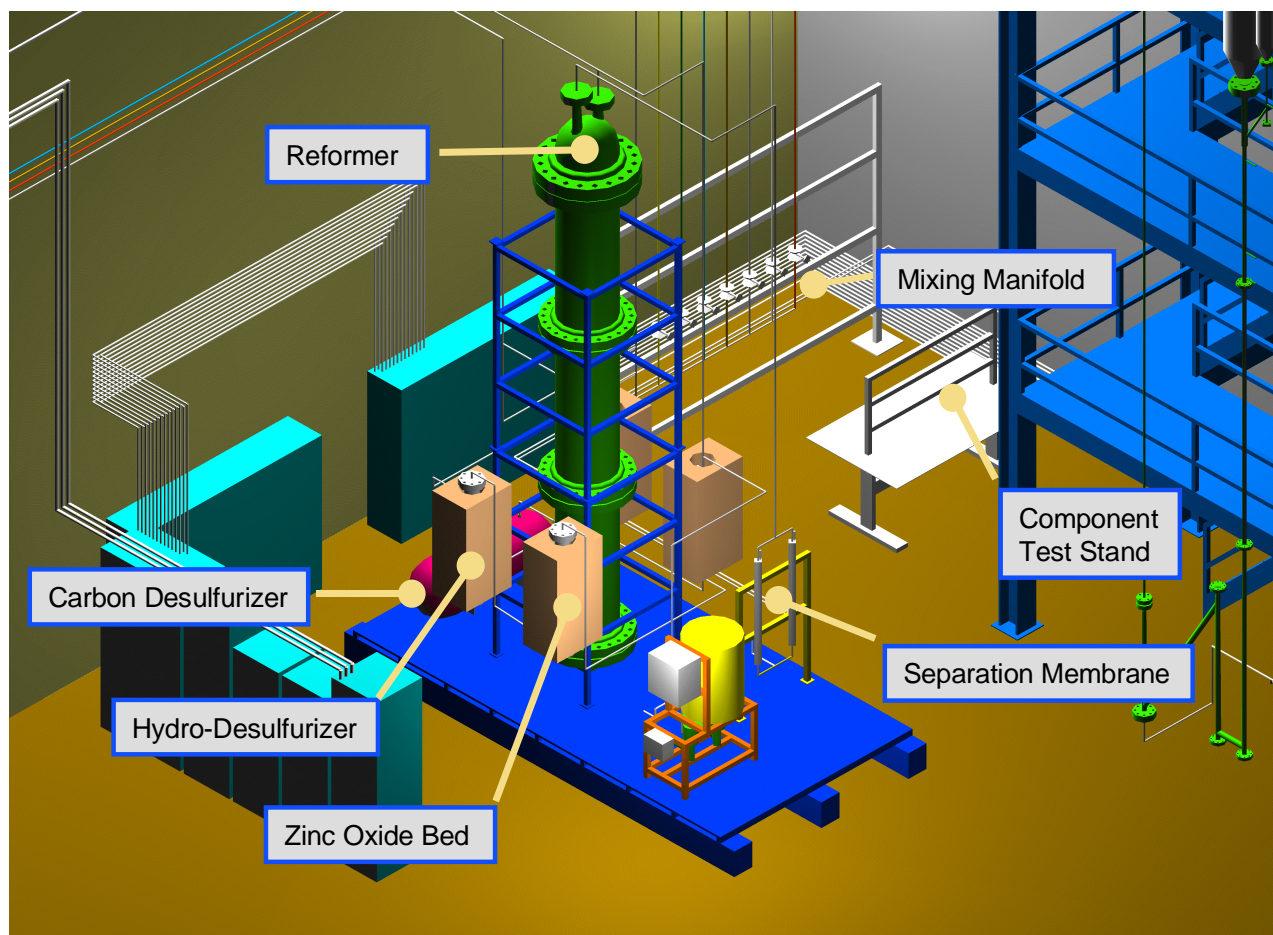


Figure 1 : Fuel Processing Research Facility

The other major activity being undertaken is completion of the Fuel Processing Laboratory (FPL). Multiple micro- and mini-scale reactors are being planned for this laboratory to conduct fundamental catalyst R&D and serve as a test and evaluation center for fuel processing technology being developed in the program.

RESEARCH OBJECTIVES: The FPRF was designed to explore R&D issues and to demonstrate technology options for fuel-gas processing at a significant scale. This team has targeted the following areas to be within the scope of fuel processing: (1) coal-gas cleanup, (2) natural gas and liquid fuel cleanup/reforming, and (3) hydrogen separation. If funding and personnel resources increase significantly, synthetic fuels and chemicals production (e.g., Fischer-Tropsch processes) could be added to the scope of the FPRF. The two principle product lines that support construction of this facility, Gasification Technology and Fuel Cell product lines, share a common syngas generator which produces a clean synthesis gas that can be tailored to the gas composition of interest. The facility is capable of processing 2,000 scfh of gas flow in an attempt to provide meaningful data beyond the lab- or bench-scale that can be more readily translated to commercial-scale operations.

LONG TERM GOALS / RELATIONSHIP TO NETL'S PRODUCT LINE(S): The FPRF will provide long-term support of NETL's Gasification Products and Fuel Cell Product Lines.

For Gasification Products, a shift from electric power-only systems to systems that provide for fuels and chemicals have necessitated another look at syngas processing needs. Cleanup of several compounds (including sulfur) will require removal to the ppbv range to satisfy syngas catalyst and membrane separation requirements. The shift towards chemicals and fuels will require continued reactor and catalyst technology support, especially as Vision 21 concepts are developed.

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ACCOMPLISHMENTS / RESULTS: The following is a brief list of project accomplishments for the FPRF and the FPL in FY01:

FPRF

- Design, construction, and installation of 12 major vessels/sub-systems completed
- Installation of all substructure components completed
- Installation of 80% of the electrical subsystems
- Completion of draft form safety integrity analysis document

FPL

- Conceptual design & facility layout completed
- Microreactor procured / preliminary design of minireactors completed
- 200 AMU mass spectrometer and gas analysis subsystem procured.

PROJECT TITLE: *Sulfur Removal Technology Assessment and Development for Liquid Fuel-Based Fuel Cell Systems*

DESCRIPTION: This activity deals primarily with the processing of liquid fuels (gasoline, diesel, JP-8, military logistics fuels, etc.) for suitable use and integration with high-temperature fuel cells, particularly fuel cells developed through the SECA program. Processing of these types of fuels involves two

principle operations, sulfur removal and fuel reforming.

This work will specifically involve proof-of-concept testing for several types of sulfur removal technologies. This project will also influence design changes from an operational viewpoint. This project's goals include the investigation of liquid-liquid sulfur extraction and liquid-gas sulfur adsorption. Successful demonstration of fuel cell operation on a highly contaminated liquid fuel feedstock has not been demonstrated. However, the market for such applications is large. For example, the military is interested in such applications from 100 W to 4 MW. The automotive industry would obviously embrace such advances. Portable electronic equipment may also be a potential match for concepts generated in this project.

RESEARCH OBJECTIVES: The objectives for this project are the conversion of a liquid feedstock into a sulfur-free synthesis gas that is high in methane and/or hydrogen and carbon monoxide concentrations.

LONG TERM GOALS / RELATIONSHIP TO NETL's PRODUCT LINE(S): Fuel cells remain one of NETL's cornerstone technologies. As the technology gets closer to commercialization, cost and performance issues dealing with the fuel processor or delivery system become more important. The market entry units are projected to be fueled by natural gas for residential or dispersed power applications. Military or remote power applications will likely require the fuel cell to convert logistic fuels (i.e., diesel or jet fuel). The long-term goal of this project is to develop the fuel processing technology necessary to construct fuel processors for these applications.

ACCOMPLISHMENTS / RESULTS: A study was conducted that compared and described a broad view of technologies available or on the horizon that could be used to desulfurize hydrocarbon fuels. Special emphasis was placed on liquid hydrocarbons. How the sulfur is removed in the process greatly affects the effectiveness and complexity of the desulfurization. For example, there are various processes that both physically adsorb or chemically adsorb sulfur in the liquid fuel. For the most part, these processes tend to be somewhat slower, batchwise processes that require significant processing to regenerate back to a usable form. Other processing schemes involve the vaporization and hydrogenation of the fuel to crack the organic sulfides, which can then be absorbed by amine technology. There are many inefficiencies to this approach. For one, hydrogen must be supplied to hydrogenate the organic sulfides which are then converted to hydrogen sulfide and later removed by zinc. This is typically accomplished by separation from the reformed fuel via pressure swing adsorption (PSA). This is not only very costly, it also requires the hot reformed gas to be cooled to near ambient conditions (more heat exchangers). This and other approaches are reviewed in the study.

PROJECT TITLE: *Conceptual Design, Simulation, and Analysis of Fuel Processing Technologies for Solids State Fuel Cell Systems*

DESCRIPTION: In order for solids state fuel cell systems to demonstrate high efficiencies they must be coupled with fuel processors to a high degree of integration. The focus of this activity is the conceptualization of fuel processor designs, their steady-state simulation, and their analysis. Initial conceptual designs will reflect current infrastructure fuels such as natural gas, gasoline, and diesel. For these systems, this involves the conversion of a sulfur-containing feedstock into a sulfur-free fuel gas that is high in methane or hydrogen and carbon monoxide concentrations. Processing of logistics fuels

involves three principle operations: (1) sulfur removal to ppbv levels, (2) fuel reforming, and (3) thermal integration with the solids state fuel cell.

This work will involve the development of conceptual designs that allow for the use of liquid fuels in high temperature solid state fuel cells. Where appropriate, detailed analysis will be performed for a series of base-case conceptual designs.

RESEARCH OBJECTIVES: The objectives for this project are to develop, identify, and simulate high efficiency fuel processing / fuel cell systems that demonstrate a high degree of process integration.

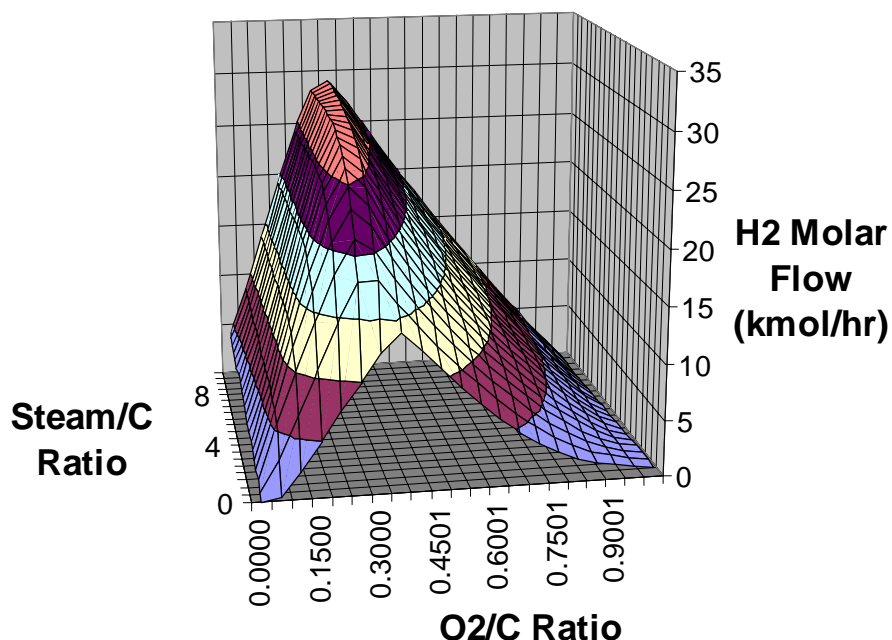
LONG TERM GOALS / RELATIONSHIP TO NETL's PRODUCT LINE(S): As the technology gets closer to commercialization, cost and performance issues dealing with the fuel processor or delivery system become more important. The market entry units are projected to be fueled by natural gas for residential or dispersed power applications. Military or remote power applications will likely require the fuel cell to convert logistic fuels (i.e., diesel or jet fuel). The long-term goal of this project is to develop the fuel processing technology necessary to construct fuel processors for these applications.

ACCOMPLISHMENTS / RESULTS: An assessment of fuel processing needs for high temperature fuel cell use as an auxiliary power unit was conducted. An innovative reactor/system configuration was developed to maximize thermal efficiency and system flexibility. General results of the study are described.

The desulfurizer temperature had a large impact on efficiency due to the extent of thermal integration that was possible. For the case where it matched the reformer temperature of 800°C (and close to the fuel cell temperature of the same), system efficiency was maximized at approximately 58%.

The reformer selected for the study was an auto thermal reactor (ATR). These reaction systems can be viewed as a balance of endothermic steam reforming reactions and exothermic partial oxidation (POX) reactions. ATR's tend to be more flexible than steam reformers and better for thermal integration than the POX reactor for the system chosen. A number of sensitivity analyses were conducted to examine the effect of variables such as fuel/air ratio, fuel/steam ration, and temperature. Some results of the study are indicated in the table and figure below:

H2 Molar Flow vs. O2/Steam/C Ratio with NO Heat Addition



PROJECT TITLE: *Simulation and Modeling of Transport Desulfurizers*

DESCRIPTION: Gas cleanup continues to be a major area of concern and emphasis. The Gasification Technology Product Team is currently promoting the use of transport reactors for gas desulfurization. Various zinc-based sorbents have been formulated and shown to be reactive enough to meet the DOE target of 1/10 of new source performance standards. However, very little attention has been paid to process development. In order to successfully develop adequate sorbents, the requirements of the process must be fully understood and determined to tailor and finalize the sorbent to be utilized. Chemical (reactivity & capacity) and physical (attrition) requirements have not been adequately addressed at the process level. For economics to be justifiable, sorbents must last thousand of cycles,

Desulfurizer Temperature	150/400 C	800 C
Efficiency	55.82	58.09
Net Power Output	5 kW	5 kW
Mass Specific Fuel Consumption	.75E-3 kgmol / kW hr	.722E-3 kgmol / kW hr

and little if any testing or characterization has been demonstrated to date. In addition to desulfurization, other gas cleanup can be accomplished in a transport reactor. As Vision 21 concepts ratchet down emissions into the ppbv levels, it becomes even more important to understand and be able to predict performance of these transport systems in order to provide developmental guidance as well as program direction. Development of the transport reactor performance model will greatly lend itself to that end. Being able to predict performance could save millions of dollars on development and test activities for desulfurization technology.

RESEARCH OBJECTIVES: The objective of this project is to develop kinetic data and reaction rate data for zinc-based sorbents to aid in understanding their capability and developing a chemical reaction rate model to be coupled with existing hydrodynamic models in the ultimate development of a reactor performance model for transport desulfurizers. Successful completion of this project will allow NETL to baseline sorbent and reactor performance against other alternatives and to more accurately model transport gas cleanup processes.

LONG TERM GOALS / RELATIONSHIP TO NETL'S PRODUCT LINE(S): This project directly supports the Gasification Products Product Line. The long-term goal is to develop a reactor performance model for transport desulfurizers that can be used for technology assessment and aid developers in scaling-up and predicting performance of commercial systems.

ACCOMPLISHMENTS / RESULTS:

In order to properly conduct this project, the following activities need to be successfully undertaken:

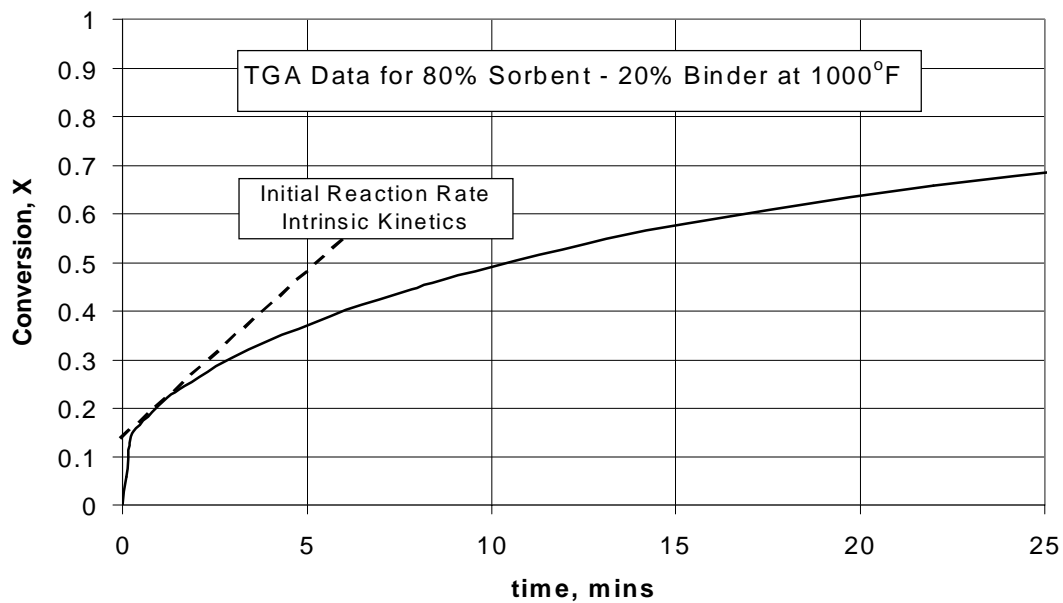
- Intrinsic kinetics need to be determined
- Mechanisms of gas/solid reaction chemistry must be understood
- Reactor performance models must be developed and validated

A series of detailed intrinsic kinetic measurements on zinc oxide was completed. Measured activation energies are in good agreement with Lew et al. (DE92-004184).

- E_a (Lew et al.) = 10,300 cal/mol
- E_a (current work) = 11,280 cal/mol

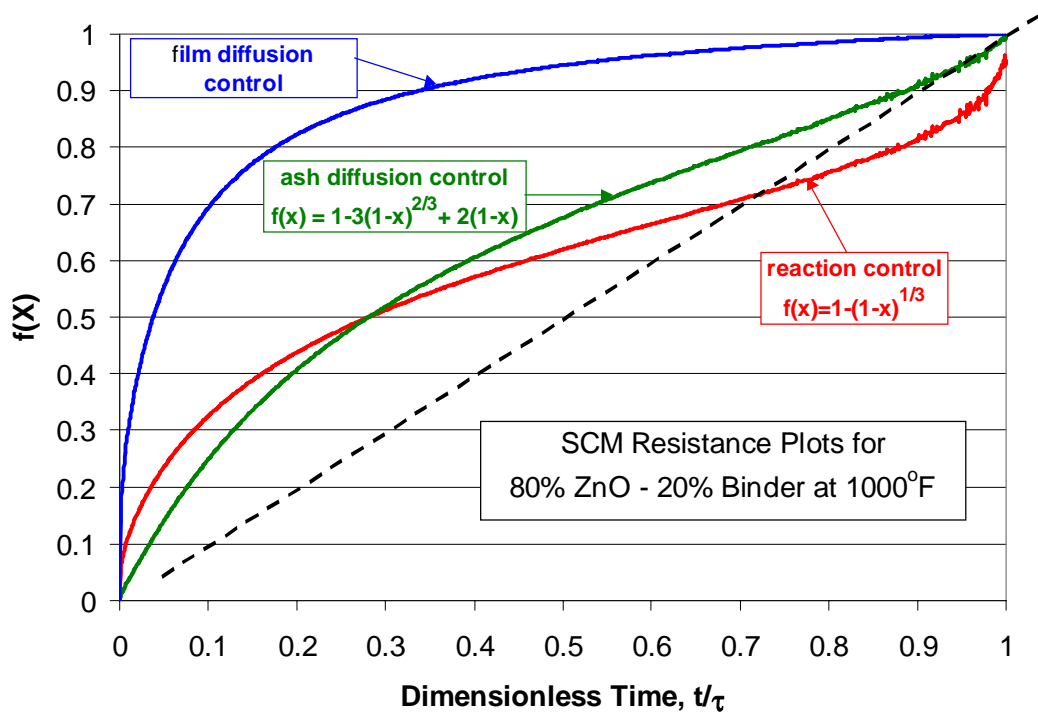
The values were developed with a thermogravimetric analyzer by utilizing very small zinc oxide particles and a constant concentration of reacting hydrogen sulfide gas. Even still, gas/solid particle reaction phenomena (such as mass diffusion) appeared to effect the reaction rate (see graph on next page). To obtain intrinsic rates and activation energies, only the initial rate was used in the determination.

It was obvious from the data that even the small micron size sorbent particles were subject to more than just intrinsic reaction rates. To help understand what is actually going on, several kinetic models were assumed. One of the models that has been proposed by various researchers to describe the phenomenon is the shrinking core model (SCM). The SCM can be thought to consist of 3 resistances in series: reaction control, ash control, and film control. Domination of any one of these resistances should result in a straight line. It is apparent from the data plotted below that no one resistance can account for the performance, and additional work needs to be done to more fully understand this system.



PROJECT TITLE: *Selective Catalytic Oxidation of Hydrogen Sulfide (SCOHS) from Coal-gas for Direct Sulfur Removal / Production*

DESCRIPTION: It is desirable to develop technology which is inherently simpler, more efficient, and less capital intensive than the current best available gas sweetening systems. The concept under investigation is the SCOHS simultaneous coal gas desulfurization and direct sulfur production. This



technology integrates gas conditioning and gas treating into a single step through the reaction pathway shown in Reaction (1):



$$\Delta G^{480^\circ F} = -177.1 \text{ KJ/mol (n=1)}$$

$$\Delta H^{480^\circ F} = -215.7 \text{ KJ/mol (n=1)}$$

The literature has indicated that this reaction will proceed selectively toward elemental sulfur between 100 and 480°F. However, 480°F is too high a temperature for a fuel gas containing carbon monoxide due to carbonyl sulfide formation. Our research this year has shown that 280°F to 350°F is the optimal temperature range for a CO-containing fuel gas. This temperature range allows us to take advantage of the higher activation energy, and correspondingly faster kinetics, necessary for the selective oxidation of hydrogen sulfide over hydrogen and carbon monoxide coal synthesis gas components. Autoignition temperatures, which are a reflection of a gas components natural ability to be oxidized are: hydrogen

is 968 °F, carbon monoxide is 1292 °F, and hydrogen sulfide is 500°F (NFPA 479, 1997). With the presence of a catalyst the selectivity of oxygen toward hydrogen sulfide can be 100%.

Recently obtained thermodynamic analyses by Paskall (1979) have shown through free energy minimization calculations, which take into account sulfur vapor-liquid-equilibrium (VLE), that Reaction (1) has the ability to convert greater than 98.5 percent (at 480°F) of the hydrogen sulfide to elemental sulfur, indicating a very high removal efficiency. The elemental sulfur produced is retained within the pores of the catalyst and may be removed through a subsequent thermal treatment.

When coupled with a zinc oxide polishing unit, this technology will have the ability to remove hydrogen sulfide to the parts-per-billion level. A guard bed will be necessary for any desulfurization process involving chemicals production due to the probability of process upset.

Early attempts to utilize this technology to clean natural gas had failed due to a selectivity problem toward higher hydrocarbons (>C5+) present in the natural gas, causing brown elemental sulfur to be produced. A derivative of this technology is currently in use, the SUPERCLAUS process, where residual sulfur dioxide is converted to hydrogen sulfide through the addition of hydrogen and subsequently reacted with oxygen via Reaction (1) to recover elemental sulfur.

The literature has indicated that the mechanism by which Reaction (1) proceeds is the Mars and van Krevelen pathway (RED-OX catalysts or *reduction-oxidation*). Many different catalysts have been used for the partial oxidation of hydrocarbons and are under investigation here. They are typically spinels of Mo-Bi, Fe-Sb, or V-Sb, and at lower temperatures activated carbon and zeolite 13X have been used. Most of the catalysts are excellent oxygen conductors. When in the presence of a combined reducing and oxidizing environment, the reduced intermediate on the catalyst (CAT - S) is 'bumped off,' in this case to form elemental sulfur. The catalyst is then re-oxidized (CAT-O), and the process repeats itself (please see P. Zenglu (1984) for details of this mechanism and Satterfield (1991) for a detailed explanation of the Mars and van Krevelen mechanism).

RESEARCH OBJECTIVES: The objectives for this project are to produce an ultra-clean syngas and by-product elemental sulfur. The general approach shall be to continue evaluating the potential of the technology through a series of carefully planned experiments. These tests will attempt to maximize sulfur production and minimize side reactions like COS and SO₂ formation. A mix of NETL and site support contractor personnel shall be utilized to accomplish the work.

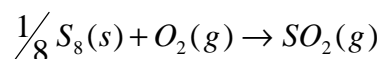
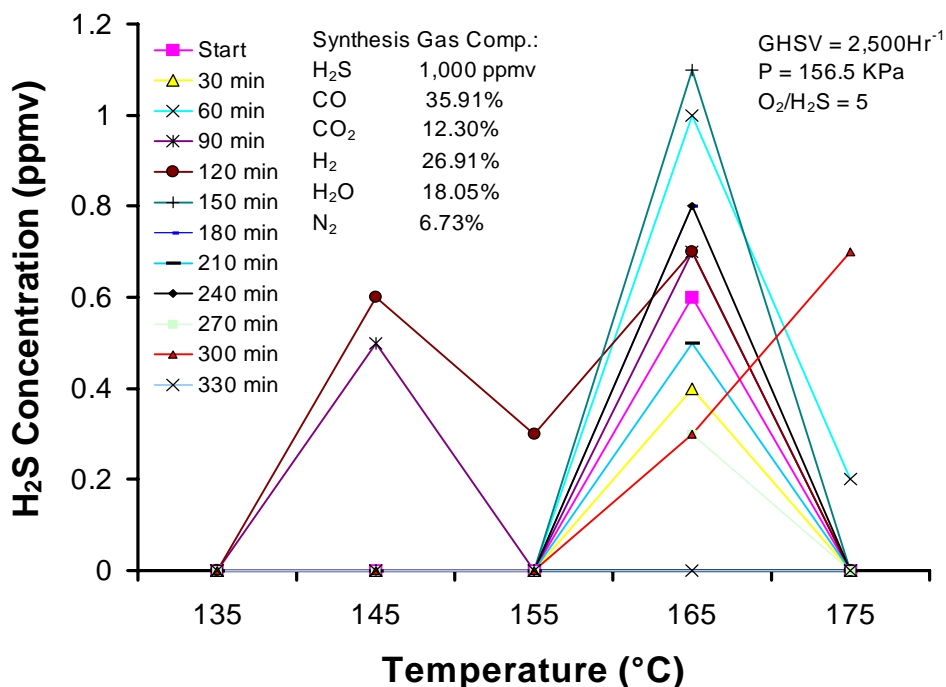
LONG TERM GOALS / RELATIONSHIP TO NETL's PRODUCT LINE(S): The degree of penetration of gasification technology into the power generation market place is highly dependent on its ability to meet ever more stringent NSPS and for its ability to produce an ultra-clean synthesis gas for tri/co-production. Central to this objective are gas conditioning and gas treating systems which are currently projected to cost as much as 15 percent of the total IGCC plant (IGCC Product Plan, 1999).

It is therefore desirable to develop technology which is inherently simpler, more efficient, and less capital intensive than the current, best available gas sweetening systems. The long-term objective of this project is to demonstrate the inherent advantages outlined above and develop the technology to the point of commercial interest and technology transfer.

ACCOMPLISHMENTS / RESULTS: A series of isothermal experiments, each timed to last exactly 5-1/2 hours, were conducted to assess the ability for a carbon-based catalyst to act as both a catalyst and a sulfur-retaining sorbent. Each timed run was conducted at a different temperature: 135, 145, 155, 165 and 175 °C. Figure 1 illustrates the ability for this catalyst to remove sulfur levels in a simulated Texaco O₂-blown gasifier gas laden with 1,000 ppmv H₂S. For this series of experiments, H₂S levels were consistently removed down to levels below 1.2 ppmv. The experiments were conducted at a GHSV of 2,500 hr⁻¹ and with an O₂/H₂S ratio of 5:1. The addition of excess oxygen was necessary to minimize the side reaction between CO and sulfur vapor to form COS.

Figure 1. H₂S exit concentration

Figure 2 illustrates that elemental sulfur trapped within the pores of the catalyst may be over oxidized to SO₂ via the reaction:



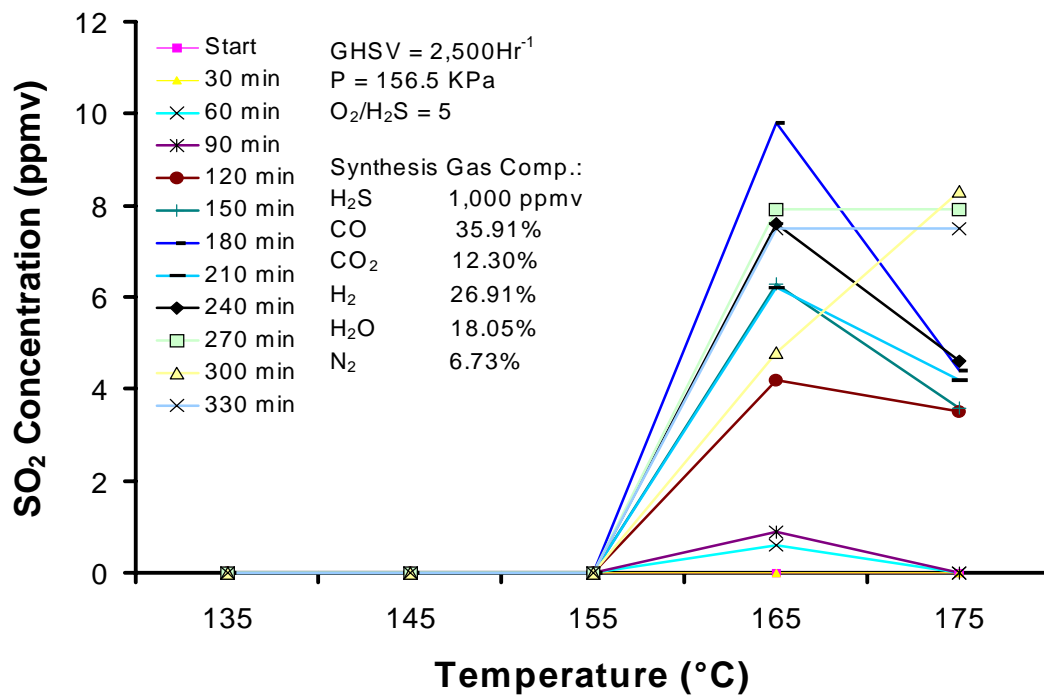
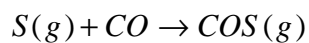


Figure 2. SO₂ exit concentration

For this catalyst, SO₂ formation was not observed below 155 °C. Therefore, utilization of this technology, using this catalyst, would be restricted to a maximum operation temperature of 155 °C.

Another possible undesirable side product is the formation of COS (Figure 3) via the reaction:



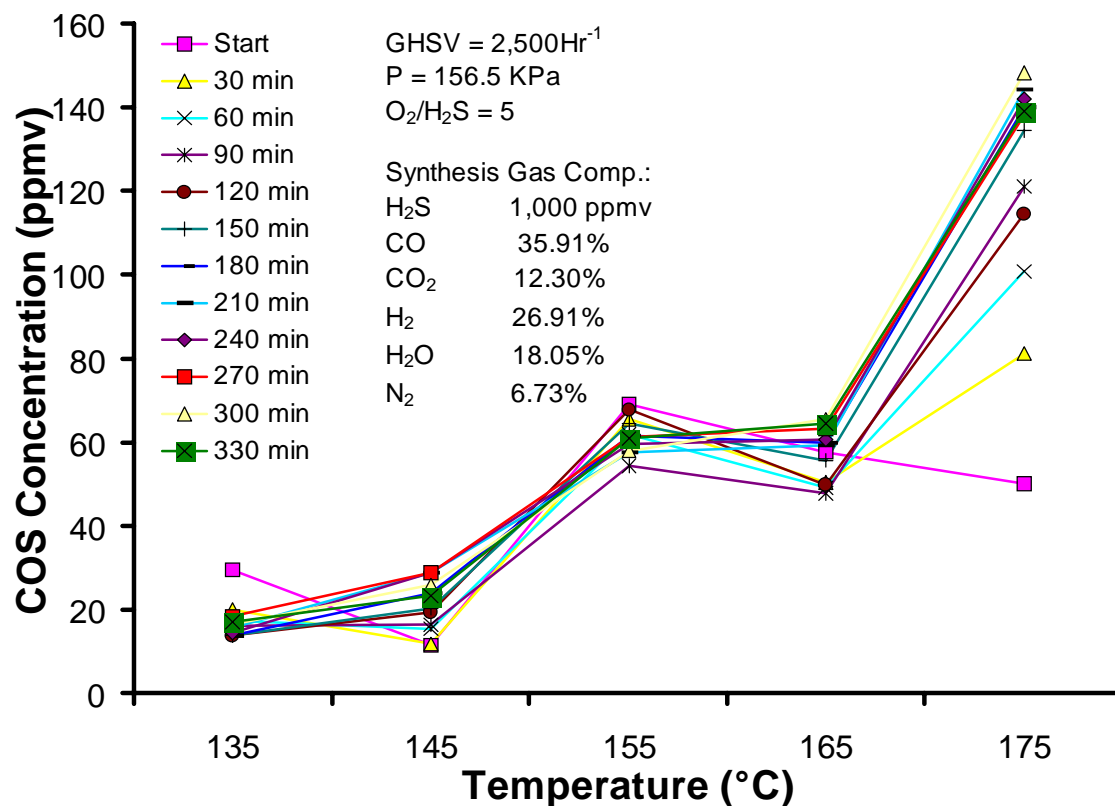


Figure 3. COS exit concentration

The strong functionality of COS formation with temperature is indicative of sulfur vapor reacting with the CO. As reaction time on stream increases and the sulfur loading of the catalyst increases, the micropores fill first. As mentioned earlier, the 5:1 ratio of O₂/H₂S was necessary to mitigate Reaction (3) from occurring. The carbon-based catalyst tested here possesses a greater affinity for O₂ over CO resulting in a displacement of CO on its surface. This, in turn, results in lower COS levels. To maintain COS levels below 20 ppmv, a maximum operation temperature below 145 °C must be maintained.

A preliminary systems analysis of the SCOHS process was also conducted to evaluate its potential for gasification (Rutkowski et al., 2001). As a baseline case the IGCC plant located at Tampa, FL (TECO) was utilized to develop a normalized comparison between cold gas cleanup and SCOHS. These preliminary results indicate that approximately a 7% reduction in the COE (\$/MWh) could be achieved if the SCOHS process were employed in lieu of an amine unit with a Claus treatment plant.

In summary, the concept of SCOHS is currently under investigation for its ability to remove H₂S to very low levels. With the carbon-based catalyst system utilized in this series of tests, side reactions become more prevalent as temperature is increased, and COS evolution becomes more significant as the catalyst sulfur loading is increased. The capillary pressure from the catalyst's micropores may play a role in mitigating this side reaction. Total sulfur levels below 20 ppmv are achievable with the current catalyst

at temperatures of 145°C and below. The elemental sulfur that is retained within the catalyst follows a sharp interface progression indicating that the global kinetics are intra-particle diffusion controlled. A highly preliminary economic analysis of the SCOHS process indicates a 7% decrease in the COE (\$/MWh) is possible if this technology is incorporated into IGCC relative to using cold gas cleanup technology.

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FOR MORE INFORMATION:

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